

US 6,951,894 B1

51

ratio between isocyanate-terminated perfluoropolyether and hydroxypropyl-terminated polysiloxane being 2:3. After the reaction has been completed and the solvent has been removed, microtitration shows a content of 0.2 meq/g of hydroxyl groups (theory 0.18 meq/g).

The third step of the synthesis described under Example B-1 is likewise carried out analogously, IEM being employed in a precisely stoichiometric ratio. After the reaction, free isocyanate groups can no longer be detected (detection limit 0.01 meq/g). 0.19 meq/g of methacryl groups are found (theory 0.19 meq/g).

EXAMPLE B-5

Production of Contact Lenses

13.0 g of macromer from Example B-1 are dissolved in 5.6 g of ethanol (Fluka, puriss. p.a.) (70% by weight solution). After complete homogenization of the solution, 5.2 g of 3-tris(trimethylsiloxy)silylpropyl methacrylate (TRIS from Shin-Etsu, product No. KF-2801), 7.8 g of freshly distilled dimethylacrylamide (DMA) and 160 mg of photoinitiator Darocur® 1173 (Ciba) are added. This solution is filtered through a Teflon membrane having a pore width of 0.45 µm under an argon pressure of from 1 to 2 atm. The filtered solution is frozen in a flask in liquid nitrogen, the flask is evacuated under a high vacuum, and the solution is returned to room temperature with the flask sealed. This degassing operation is repeated twice. The flask containing the macromer/comonomer solution is then transferred into a glove box with an inert-gas atmosphere, where the solution is pipetted into dust-free contact-lens moulds made from polypropylene. The moulds are closed, and the polymerization reaction is effected by UV irradiation (15 mW/cm², 5 min.), with simultaneous crosslinking. The moulds are then opened and placed in ethanol, causing the resultant lenses to swell out of the moulds. The lenses are extracted for 24 hours with constantly replenished distilled dichloromethane and subsequently dried in a high vacuum. The dried lenses are equilibrated in phosphate-buffered physiological saline solution in autoclave-resistant vials and then autoclaved at 120° C. for 30 minutes. All physical data measurements are carried out on autoclaved lenses.

The lenses produced in this way are characterized by the following values: oxygen permeability (Dk) 77 barrer (determined by the "wet" method described below), water content of the equilibrated lenses 32 percent by weight, elongation at break at 35° C. 360%, modulus of elasticity 30° C. 0.5MPa (measured using a Minimat from Polymer Laboratories, UK).

"Wet" measurement of the oxygen permeability

The oxygen permeability of a material is determined by the coulometric method. To this end, pre-autoclaved lenses are clamped in a holder and then covered on the upper side with a 2cm layer of water. A gas mixture comprising 21% of oxygen and 79% of nitrogen is passed continuously through the water layer with swirling. The oxygen which diffuses through the lens is measured using a coulometric detector. The reference values are those measured on commercially available contact lenses using this method. Cibasoft/(CIBA-Vision, HEMA lens) gives a measurement of approx. 7–10 barrer, and Excelens/(CIBA-Vision, PVA lens) gives a measurement of approx. 22 barrer.

Unfortunately, the oxygen permeability of, for example, contact lenses is frequently given to in the literature as a straight Dk value without further definition and frequently without giving any reference material. These are usually

52

values determined on dry material (dry measurement). A comparative measurement of the oxygen permeability of polymer B-5 shows the differences:

- a) "wet" measurement: 77 barrer
- b) dry measurement: 158 barrer

EXAMPLE B-6

The process described under Example B-5 for the production of contact lenses is repeated, but the mixture of comonomers has the following composition (in per cent by weight):

- 55% of macromer from Example B-1
- 22% of TRIS
- 22.5% of DMA
- 0.5% of Blemer® QA

EXAMPLE B-7

The process described under Example B-5 for the production of contact lenses is repeated, but the mixture of comonomers has the following composition (in per cent by weight):

- 55% of macromer from Example B-1
- 22% of TRIS
- 23% of DMA

EXAMPLE B-8

Analogously to EXAMPLE B-5 (in weight percent):

- 40% of macromer from Example B-1
- 30% of TRIS
- 30% of DMA

EXAMPLE B-9

The process described under B-5 for the production of contact lenses is repeated, but a 70% by weight solution of the macromer in toluene is used instead of the 75% by weight solution in ethanol described above. The mixture of comonomers has the following composition (in per cent by weight):

- 55% of macromer from Example B-1
- 22% of TRIS
- 23% of DMA

EXAMPLE B-10

The process described under B-5 for the production of contact lenses is repeated, but a 70% by weight solution of the macromer in octamethylcyclotetrasiloxane is used instead of the 75% by weight solution in ethanol described above. The mixture of comonomers has the following composition (in per cent by weight):

- 55% of macromer from Example B-1
- 22% of TRIS
- 23% of DMA

Physical measurement data for the contact-lens materials from Examples B-5 to B-10 (O₂Dk value, wet method) are presented in TABLE B-I:

US 6,951,894 B1

53

TABLE B-I

Example	Water Content [%]	Dk [barrer]	Modulus of Elasticity [MPa]	Elongation at Break [%]
B-5	32	77	0.5	360
B-6	23.8	110	1.1	160
B-7	19.5	110	0.6	130
B-8	30.9	81	0.3	300
B-9	30			
B-10	25			

EXAMPLE B-11

About 10.0 grams of macromer from Example B-1 are dissolved in 3.3 grams of ethanol (Fluka, puriss. p.a.). After complete homogenization of the solution, about 4.0 grams of 3-tris(trimethylsiloxy)silylpropyl methacrylate (TRIS from Shin-Etsu, product no. KF-2801), about 5.9 g. freshly distilled dimethylacrylamide (DMA), about 0.1 g. Blemer® QA (a methacrylate having quaternary ammonium substituents, Linz Chemie) and about 100 mg of photoinitiator Darocur® 1173(Ciba) are added. The solution is filtered through a TEFLON membrane having a pore width of 0.45 mm under an argon pressure of from about 1 to 2 atm.

The filtered solution is frozen in a flask in liquid nitrogen, the flask is evacuated under a high vacuum, and the solution is returned to room temperature with the flask sealed. This degassing operation is repeated twice. The flask containing the macromer/comonomer solution is then transferred into a glove box with an inert gas atmosphere, where the solution is pipetted into dust-free, polypropylene contact lens molds. The molds are closed, and the polymerization reaction is effected by UV irradiation, with simultaneous crosslinking. The molds are then opened and placed in isopropyl alcohol, causing the resultant lenses to swell out of the molds. The lenses are extracted for about 24 hours with nearly continuous replenishing of isopropyl alcohol. Subsequently, the lenses are dried under high vacuum.

The dried contact lenses are equilibrated in autoclave-resistant vials in phosphate-buffered physiological saline solution, and then autoclaved for 30 minutes at about 120° C. Physical measurement data for the autoclaved lens is presented below:

Dk [barrer]:	93
water content [%]:	20.3%
modulus of elasticity [Mpa]:	0.96

EXAMPLE B-12

Lenses are prepared in accordance with the procedures described in Example B-11, but are subsequent surface treated as follows. The dried lenses are transferred into a plasma coating apparatus wherein they are surface treated in a methane/“air” mixture (“air” as used here, denotes 79% nitrogen and 21% oxygen) for a period of about 5 minutes. The apparatus and plasma treatment process have been disclosed by H. Yasuda in “Plasma Polymerization” Academic Press, Orlando, Fla. (1985), pages 319 forward.

The plasma-treated contact lenses are equilibrated in autoclave-resistant vials in phosphate-buffered physiological saline solution, and then autoclaved for 30 minutes at

54

about 120° C. Physical measurement data for the plasma-coated autoclaved lens is presented below:

Dk [barrer]:	88
water content [%]:	21.8%
modulus of elasticity [Mpa]:	1.03

EXAMPLE B-13

Lenses are prepared in accordance with the procedures described in Example B-5, but the mixture comonomers has the following composition, in weight percentages:

Macromer of Example B-1:	60%
TRIS:	25%
DMA:	15%

EXAMPLE B-14

Lenses are prepared in accordance with the procedures described in Example B-6, with the same comonomer composition, but the comonomers are dispensed into dust-free contact lens molds in ambient air atmosphere.

EXAMPLE C-1

Reaction of α,ω -bis-aminopropyl-dimethylpolysiloxane with D(+)-gluconic acid d-lactone:

Before the reaction, the amino-functionalized polydimethylsiloxane employed for the synthesis (X-22-161-C, Shin Etsu, JP) was finely dispersed in acetonitrile, extracted and then subjected to molecular distillation.

The following reactions take place with exclusion of H₂O. 200 g of purified amino-functionalized polydimethylsiloxane (0.375 meq of NH₂/g; Mn(VPO) 3400–3900(VPO, Vapour Pressure Osmometry)), dissolved in 200 ml of absolute THF, are slowly added dropwise to a suspension of 13.35 g (75 mmol) of D(+)-gluconic acid d-lactone in 50 ml of absolute THF and the mixture is stirred at 40° C. for about 24 hours until the lactone has reacted completely. (Monitoring of the reaction by thin layer chromatography (TLC): silica gel; i-propanol/H₂O/ethyl acetate 6:3:1; staining with Ce(IV) sulfate/phosphoromolybdic acid solution (CPS reagent)). After the reaction, the reaction solution is concentrated to dryness and the residue is dried under 3 Pa (0.03 mbar) for 48 hours. 213.3 g of α,ω -bis(3-gluconamidopropyl)-poly-dimethylsiloxane are obtained. Titration of the amino groups with perchloric acid shows a conversion of the amino groups of more than 99.8%.

Reaction of α,ω -bis-3 gluconamidopropyl-dimethylpolysiloxane with IEM The product obtained above (213.3 g) is dissolved in 800 ml of absolute THF and the solution is heated to 40° C. with the addition of catalytic amounts of dibutyltin dilaurate (DBTDL). 14 g (90 mmol) of IEM in 20 ml of absolute THF are added dropwise to this solution over a period of about 4 hours. This corresponds to a concentration of 1.2 equivalents of IEM per gluconamide unit. The reaction is carried out in the course of 48 hours (monitoring of the reaction by IR spectroscopy detection of the NCO ties). The reaction solution is concentrated and the product is dried in a brown glass flask under 3 Pa (0.03 mbar) for 24 hours, while cooling with ice. 227.2 g of a colourless rubber-elastic product of high optical transparency remain.

US 6,951,894 B1

55

EXAMPLE C-2 to C-7

Further amino propyl-dimethylpolysiloxanes (PDMS) are reacted with a different amount of gluconolactone and concentrations of IEM analogously to Example C-1. The examples are summarized in Table C-I.

56

EXAMPLE C-12

52.09 g (9.78 mmol) of purified amino-functionalized polydimethylsiloxane (X-22-161-C, Shin Etsu JP), dissolved in 110 ml of absolute THF, are initially introduced into the reaction vessel under an inert gas atmosphere, and

TABLE C-I

Example	Poly(dimethyl siloxane) [PDMS]				Amount of batch		
	Name	Type	Mn	NH ₂ * of NH ₂	PDMS g(mmol)	Glu g (mmol)	IEM g (mmol)
C-1	X-22-161-C	term.	3400	2	200 (75)	13.4 (75)	14.0 (90.0)
C-2	X-22-161-C	term.	3400	2	200 (74)	13.4 (75)	25.7 (165.0)
C-3	X-22-161-C	term.	3400	2	200 (75)	13.4 (75)	29.2 (187.5)
C-4	PS 813	pen.	1200	1			
C-5	GP 4	pen.	3150	2.6			
C-6	GP 6	pen.	5960	3			
C-7	KF 8003	pen.	9700	4.7	200 (98)	17.5 (98)	18.2 (117.4)

Legend:

X-22-161-C and KF 8003 are products from Shin Etsu (Japan), PS813 is a product from Petrarch-H ls, GP4 and GP6 are products from Genesee.

*Amino groups per macromer chain

Glu: D(+) gluconic acid d-lactone

term: terminal

pen: pendent

EXAMPLE C-8

The reaction is carried out in accordance with Example C-1, but instead of D(+)gluconic acid d-lactone, 75 mmol of lactobionic acid 1,5-lactone, suspended in 50 ml of absolute THF, are added dropwise to a solution of amino-functionalized polydimethylsiloxane (X-22-161 -C) in 180 ml of absolute THF and 20 ml of DMSO (pure, 99%). Titration of the amino groups with perchloric acid indicates a reaction conversion of 99% (<0.01 meq of NH₂/g). Here also, a colourless optically clear macromer is obtained.

EXAMPLE C-9 and C-10

The reactions are carried out analogously to Example C-1. However, the catalyst necessary for addition of the isocyanate onto the hydroxyl groups is varied. Instead of DBTDL, catalytic amounts of 1,4-diazabicyclo[2.2.2]octane (DABCO) or 4-dimethylamino-pyridine (DMAP) are added and the reaction is continued as described under Example C-1. In both cases, an optically clear, colourless rubber-elastic macromer results in a manner corresponding to Example C-1.

EXAMPLE C-11

The reaction is carried out analogously to Example C-1. In a manner corresponding to Example C-8, 0.1 mol of lactobionic acid 1,5-lactone is suspended in 50 ml of absolute THF and the suspension is added dropwise to a solution of amino-functionalized polydimethylsiloxane (KF-8003) in 180 ml of absolute THF and 20 ml of DMSO (pure, 99%). The reaction time is increased to about 48 hours. A residual content of 0.07 meq of NH₂/g can be detected, and is reacted completely by addition of the corresponding molar amount of D(+)gluconic acid d-lactone to the reaction solution. The colourless highly transparent product has a residual content of amino groups of <0.01 meq/g.

1.14 g (6.52 mmol) of D-glucaro-1,4:6,3-dilactone, dissolved in 20 ml of absolute THF, are added. The reaction solution is stirred at room temperature for 15 hours and then worked up in a manner corresponding to Example C- 1. The amine content is 0.134 meq/g. The terminal amino groups of the resulting penta-block macromer are reacted with gluconolactone in the following reaction step. 41.84 g (5.146 meq of NH₂) of the above macromer and 0.917 g (5.15 mmol) of D(+)gluconic acid d-lactone are suspended in 300 ml of absolute THF and the suspension is stirred under nitrogen at 40° C. for 18 hours. The filtered solution is then concentrated and the residue is dried under 3 Pa (0.03 mbar) for 48 hours. A highly viscous optically clear substance having a residual content of amino groups of 0.013 meq/g results.

EXAMPLE C-13

Preparation of an amino- and perfluoroalkyl-functionalized polydimethylsiloxane:

3.0 ml of absolute toluene are added to 15 g of poly (dimethylsiloxane-co-methylhydrosiloxane) [Bayer Silopren U-230; 10,000 g/mol; 2.3 mmol of Si-H/g], and 1.72 g (9.2 mmol) of allylphthalimide [CAS Reg. No. 5428-09-1] are then added. The mixture is frozen several times and the flask evacuated and then brought to room temperature again. The flask is then let down with argon. 0.7 ml of a 0.005 molar solution of Lamnorea catalyst (prepared in accordance with U.S. Pat. No. 3,220,972, General Electric) in absolute toluene (100 ppm of Pt/mol of Si-H) is added and the mixture is heated to 80° C. After a reaction time of half an hour, a colourless, clear to slightly cloudy solution, the ¹H—NMR spectrum of which no longer shows resonances of allylic hydrogen atoms, is obtained.

Thereafter, 6.2 g (15.3 mmol) of degassed allyl 1H,1H, 2H,2H-perfluorooctyl ether are slowly added and the mixture is stirred at 80° C. for 2 hours. A ¹H—NMR spectrum now shows a severely weakened resonance of the Si-H

US 6,951,894 B1

57

function at 4.6 ppm and an intense resonance at 0.5 ppm, which originates from Si—CH₂ hydrogen atoms.

3.0 ml of 1-hexene are then added in order to react the remaining excess of Si—H groups, which could otherwise cause crosslinking of the polymer when air later has access. The mixture is further stirred at 80° C. for another half an hour. The reaction mixture is then left to stand overnight. The product is purified over a silica gel column with hexane/ethyl acetate (3:2), the solvent is stripped off and the macromer is dried under a high vacuum. A colourless, clear, viscous product is obtained. The macromer purified in this way is taken up in 20 ml of hexane, 20 ml of methylamine [33% in ethanol] are added and the mixture is heated to 40° C. After 10–15 minutes, a white voluminous precipitate separates out. After 30 minutes, the suspension is cooled and filtered and the precipitate is washed with a little hexane. The filtrate is evaporated and the residue is then dried under a high vacuum. Thereafter, the content of amino groups is determined by titrimetry (perchloric acid).

The resulting macromer is clear and viscous. The amino group content is 78.6% of theory. The total yield of macromer after the chromatographic purification is 75%.

Preparation of a gluconamide:

17.3 g (corresponding to an amine content of 5.4 meq) of this aminoalkyl-substituted product are dissolved in 20 ml of dried THF. The solution is repeatedly frozen, degassed and let down with argon. All the following operations are carried out in an argon atmosphere. 712 mg of D(+)-gluconic acid d-lactone (4 mmol) are then added. Because of the low solubility of the lactone, a suspension is initially obtained. After stirring overnight at 50° C., the solution is clear and the lactone has been used completely. The stoichiometric remaining amount of D(+)-gluconic acid d-lactone (260 mg, 1.46 mmol) is then added and the mixture is stirred again at 50° C. overnight. A trace of unreacted lactone is observed.

58

hour, while cooling with ice 1.44 g of macromer from Example C-1 are transferred to a round-bottomed flask with a nitrogen attachment, degassed under 3 Pa (0.03 mbar) for 24 hours and then dissolved in 2.7 g of ethanol which has been flushed with N₂ for half an hour beforehand. The subsequent preparation of samples and the polymerization are carried out inside a glove box with exclusion of oxygen. The above monomer mixture and the macromer solution from Example C-1 are mixed, with the addition of 0.012 g (0.21 mmol) of Darocur® 1173 and the mixture is subjected to microfiltration (0.45 mm filter). 180 µl of this mixture are introduced into a polypropylene mould, which is then closed with an appropriate lid of polypropylene. The mixture is then irradiated with a UV-A mercury high pressure lamp in a nitrogen atmosphere in a UV oven equipped for this for 5 minutes. The lamps (5 each of the brand TLK40W/10R, Philips) are above and below the holder inserted. The irradiation intensity is 14.5 mW/cm².

The polypropylene mould is opened and the finished discs or lenses are removed by soaking by means of a solvent mixture of methylene chloride and ethanol (2:3). The lenses and discs are extracted in ethanol at room temperature in special polypropylene cages for 48 hours and then dried at 40° C. under 10 Pa (0.1 mbar) for 24 hours (autoclaving at 120° C., 30 minutes). The discs show an E modulus of 1.1 MPa, a permeability to oxygen of 183 barrier and a hardness (Shore A) of 53.

EXAMPLE C-15 to C-19

Further polymers are prepared in a manner corresponding to Example C-14 (composition in percentages by weight). Table C-II shows examples C-15 to C-19 and the properties of the resulting materials measured on discs.

TABLE C-II

Example	Water Content [%]	Macromer from Example	Macromer weight percent	DMA weight percent	DMEA weight percent	TRIS weight percent	E modulus [Mpa]	Dk [barrier]
C-15	not measured	C-3	32.8	—	30	37.2	—	—
C-16	19.9	C-3	32.9	34.3	—	32.7	0.7	84
C-17	25.1	C-3	39.3	34.3	—	36.4	0.9	72
C-18	17.5	C-3	35.7	34.3	—	30.0	0.7	100
C-19	23.4	C-3	33.3	33.3	—	33.4	0.7	96

Legend:

DMA: N,N-Dimethylacrylamide

TRIS: 3-Methacryloyloxypropyl-tris(trimethylsilyloxy)silane

DMEA: 2-Dimethylaminoethyl acrylate

Completion of the reaction is monitored by means of thin layer chromatography on silica gel plates with the mobile phase 1-propanol/ethyl acetate/water (6:1:3). The silica gel plates are developed by means of Ce(IV) sulfate/phosphoromolybdic acid solution. Subsequent titration on amino groups yields a residual amino content of <0.1%. After filtration and removal of the solvent by distillation, a highly viscous clear macromer with 0.295 mequivalent of gluconamide per gram of macromer is obtained.

EXAMPLE C-14

Before the polymerization, the acrylates employed, isobutyl acrylate (IBA), N,N-dimethylacrylamide (DMA) and 3-methacryloyloxypropyl-tris(trimethylsilyloxy)silane (TRIS) are each freed from inhibitors by distillation. 0.32 g (2.76 mmol) of IBA, 0.80 g (8.1 mmol) of DMA and 1.44 g (3.4 mmol) of TRIS are weighed into a 50 ml round-bottomed flask and the flask is flushed with N₂ for half an

EXAMPLE C-20

Uncoated Contact Lens

A contact lens is prepared in a manner corresponding to Example C-14, using the Example C-3 macromer, with the following composition in percentages by weight:

Macromer:	33.3
DMA:	33.3
TRIS:	33.4

The lens has a Dk of about 94 and a water content of about 20.0 weight percent. The results are presented in TABLE C-III for comparison with coated lens properties.

US 6,951,894 B1

59**EXAMPLE C-21****Plasma-treated Contact Lens**

Dried lenses prepared in accordance with the procedures described in Example C-20 are transferred into a plasma coating apparatus where the lenses are surface treated in a methane/"air" mixture ("air" as used here, denotes 79% nitrogen and 21% oxygen). The apparatus and plasma treatment process have been disclosed by H. Yasuda in "Plasma Polymerization" Academic Press, Orlando, Fla. (1985), pages 319 forward.

The dried plasma-treated contact lenses are equilibrated in autoclave-resistant vials in phosphate-buffered physiological saline solution, and then autoclaved for 30 minutes at about 120° C. The plasma-treated autoclaved lens has a Dk [barrer] of 90 and a water content of 21.5%. The results are presented in TABLE C-III for comparison with coated lens properties.

TABLE C-III

Example	Surface type	Dk [barrer]	Water content [%]
C-20	untreated	94	20.0
C-21	plasma-treated	90	21.5

EXAMPLE C-22

The synthesis of this polymer corresponds to Example C-14 with the following comonomer composition: Example C-3 macromer/TRIS/DMA: 32.8%/32.6%/34.2% (in percentages by weight) and an addition of 0.4% by weight of trimethylammonium-2-hydroxypropyl methacrylate hydrochloride (Blemer® QA, Nippon Oil Corp.). The polymer has a modulus of 0.9 MPa and a permeability to oxygen of '2 barrier. The water content is 25.1% (after 30 minutes' autoclaving at 120° C.). For comparison, Example C-16 has a water content of 20% with a very similar comonomer composition (no addition of Blemer® QA).

EXAMPLE C-23

The polymer is prepared analogously to Example C-14, but the polymerization is carried out in bulk, which means without addition of ethanol. The composition of the comonomers and the material properties of the polymer synthesized, measured on discs is given below.

Example C-7 macromer:	41%
IBA:	23%
1-vinyl-2-pyrrolidone (NVP):	24%
acrylonitrile (AN):	12%
Hardness (shore A):	68

EXAMPLE C-24

The polymerization is carried out in accordance with Example C-14 but with the following changed comonomer composition:

macromer of Example C-7/IBA/TRIS 20%/19%/60% and 1% (in percentages by weight) of bis(3-methacryloyloxypropyl)tetra methylsiloxane.

An optically clear polymer with an E modulus of 0.4 MPa, a permeability to oxygen of 241 barrier and a hardness (Shore A) of 42 is obtained.

60**EXAMPLES C-25 through C-27**

Contact lenses are prepared in accordance with the procedure described in Example C-1 4. The compositions in weight percentages are as follows:

Example	Macromer	Macromer weight percent	IBA weight percent	DMA weight percent	TRIS weight percent	HFBA weight percent
C-25	C-3	36.0	8.0	20.0	36.0	—
C-26	C-2	35.0	5.0	20.0	35.0	5.0
C-27	C-3	32.8	—	30.0	37.2	—

where

IBA is isobutylacrylate,

DMA is N,N-Dimethylacrylamide

TRIS is 3-methacryloyloxypropyl-tris(trimethylsiloxy)silane

HFBA is acrylsäure-2,2-3,4,4,4-hexafluorbutylester

EXAMPLE C-28

The polymerization is carried out in accordance with Example C-14 but with the following changed comonomer composition: macromer of Example C-1/DMA/TRIS 33.3%/33.3%/33.3%. An optically clear polymer is obtained.

EXAMPLE D-1**Macromer Synthesis**

In a dry box under nitrogen atmosphere, about 200 grams of dry PDMS dipropoxyethanol (Shin-Etsu) is added to a container. Isocyanatoethyl methacrylate (IEM) in an amount equal to about 2 moles per mole PDMS dialkanol is added to the container. About 0.1 weight percent dibutyltin dilaurate (DBTL) catalyst, based on PDMS dialkanol weight, is added to the container along with a stir bar. The container is immersed in an oil bath atop a stir plate, and secured in place with a clamp. A stream of UPC air at about 2 psig is passed over the mixture. The mixture is agitated at room temperature (about 22° C.) for about 24 hours. An iterative procedure follows in which the mixture is analyzed for isocyanate content and IEM is added if the PDMS dialkoxyalkanol has not been completely reacted. The mixture is stirred about 24 hours more. The macromer produced is a siloxane-containing macromer.

EXAMPLE D-2**Lens Fabrication**

A prepolymerization mixture is prepared by mixing about 56 grams of the macromer from Example D-1, about 14 grams of TRIS about 29 grams N,N-dimethylacrylamide (DMA), about 1 gram methacrylic acid, about 0.5 grams Darocur® 1173 photoinitiator, and about 20 grams hexanol. The mixture is agitated for about 20 minutes at room temperature.

Next, the mixture is degassed via a series of freezing and thawing steps. The container is placed in a liquid nitrogen bath until the mixture solidifies. A vacuum is applied to the container at a pressure of about 200 millitorr or less for about 5 minutes. Then, the container is placed in a bath of room temperature water until the mixture is liquid again. This process is performed a total of three times.

US 6,951,894 B1

61

The mixture is then polymerized to form contact lenses. The prepolymerization mixture is poured into polypropylene contact lens molds in a nitrogen atmosphere. The polymerization is effected by applying UV radiation (about 4–6 mW/cm²) for a period of about 15 minutes.

The resulting fully hydrated contact lens has a water content of about 23%. The lens has a Dk of about 115 barrers and a modulus of elasticity of about 2 MPa.

EXAMPLE D-3**Lens Fabrication**

A contact lens is prepared in accordance with the procedure described in Example D-2, with the difference being that the composition is about 50% macromer of Example D-1, about 20% TRIS and about 30% DMA.

The resulting fully hydrated contact lens has a water content of about 20%. The lens has a Dk of about 118 barrers and a modulus of elasticity of about 1.8 Mpa.

EXAMPLE E-1**Material A**

A contact lens is prepared substantially in accordance with the procedure described in Example A-2. Prior to polymerization, the prepolymerization mixture is degassed by cooling the prepolymer mixture with liquid nitrogen until the mixture solidifies and is near liquid nitrogen temperature, then applying a vacuum (about 0.1 mm Hg) to the solidified prepolymer mixture, discontinuing the vacuum, and thawing the prepolymer mixture until the mixture is again in liquid form. This degassing procedure is performed a total of three times on the prepolymerization mixture.

The prepolymer mixture is cured in a nitrogen atmosphere to form the contact lens. The cured lens has an equilibrium water content of about 19%. Subsequent to curing, the lens is plasma treated for about 10 minutes in an atmosphere of methane and air at a 2:1 CH₄:air volume:volume ratio. The working pressure of the gas is about 50 millitorr. The plasma treatment is accomplished in a Plasma Polymerization Apparatus LCVD-20-400A (Plasmacarb, Bedford, Mass.).

The Ionoton Ion Permeability Coefficient of the lens is 0.81×10^{-3} cm²/sec. Clinical examination shows that the lens moves on the human eye. See Table E for a summary of the results.

EXAMPLE E-2**Material B**

A contact lens is prepared substantially in accordance with the procedure described in Example B-10. Prior to polymerization, nitrogen gas is bubbled through the prepolymer mixture in order to remove oxygen from the prepolymer mixture.

The prepolymer mixture is cured in a nitrogen atmosphere to form the contact lens. The cured lens has an equilibrium water content of about 26 weight percent. No coating is applied to the surface.

The Ionoton Ion Permeability Coefficient of the lens is -0.063×10^{-3} cm²/sec. Clinical examination shows that the lens does not move on the human eye. See Table E for a summary of the results.

EXAMPLE E-3**Material B**

A contact lens is prepared substantially in accordance with the procedure described in Example B-12. Prior to

62

polymerization, the prepolymerization mixture is degassed by the repeated freeze/thaw procedure of Example E-1.

The prepolymer mixture is cured in a nitrogen atmosphere to form the contact lens. The cured lens has an equilibrium water content of about 30 weight percent. Subsequent to curing, the lens is plasma treated for about 3 minutes in an atmosphere of methane and air at a 2:1 CH₄:air volume ratio.

The Ionoton Ion Permeability Coefficient of the lens is 0.50×10^{-3} cm²/sec. Clinical examination shows that the lens moves on the human eye. See Table E for a summary of the results.

EXAMPLE E-4**Material B**

A contact lens is prepared substantially in accordance with the procedure described in Example B-12. Prior to polymerization, the prepolymerization mixture is degassed by the repeated freeze/thaw procedure of Example E-1.

The prepolymer mixture is cured in a nitrogen atmosphere to form the contact lens. The cured lens has an equilibrium water content of about 30 weight percent. Subsequent to curing, the lens is plasma treated for about 5 minutes in an atmosphere of methane and air at a 2:1 CH₄:air volume ratio.

The Ionoton Ion Permeability Coefficient of the lens is 0.47×10^{-3} cm²/sec. Clinical examination shows that the lens moves on the human eye. See Table E for a summary of the results.

EXAMPLE E-5**Material B**

A contact lens is prepared substantially in accordance with the procedure described in Example B-12. Prior to polymerization, the prepolymerization mixture is degassed by the repeated freeze/thaw procedure of Example E-1.

The prepolymer mixture is cured in a nitrogen atmosphere to form the contact lens. The cured lens has an equilibrium water content of about 30 weight percent. Subsequent to curing, the lens is plasma treated for about 7.5 minutes in an atmosphere of methane and air at a 2:1 CH₄:air volume ratio.

The Ionoton Ion Permeability Coefficient of the lens is 0.35×10^{-3} cm²/sec. Clinical examination shows that the lens moves on the human eye. See Table E for a summary of the results.

EXAMPLE E-6**Material B**

A contact lens is prepared substantially in accordance with the procedure described in Example B-11. Prior to polymerization, the prepolymerization mixture is degassed by the repeated freeze/thaw procedure of Example E-1.

The prepolymer mixture is cured in a nitrogen atmosphere to form the contact lens. The cured lens has an equilibrium water content of about 30 weight percent. The lens is not subsequently coated.

The Ionoton Ion Permeability Coefficient of the lens is 1.1×10^{-3} cm²/sec. Clinical examination shows that the lens moves on the human eye. See Table E for a summary of the results.

EXAMPLE E-7**Material C**

A contact lens is prepared substantially in accordance with the procedure described in Example C-2 1. Prior to

US 6,951,894 B1

63

polymerization, the prepolymerization mixture is degassed by the repeated freeze/thaw procedure of Example E-1.

The prepolymer mixture is cured in a nitrogen atmosphere to form the contact lens. Subsequent to curing, the lens is plasma treated for about 5 minutes in an atmosphere of methane and air at a 2:1 CH₄:air volume ratio.

The Ionoton Ion Permeability Coefficient of the lens is 2.9×10^{-3} cm²/sec. Clinical examination shows that the lens moves on the human eye. See Table E for a summary of the results.

EXAMPLE E-8

Material C

A contact lens is prepared substantially in accordance with the procedure described in Example C-21. Prior to polymerization, the prepolymerization mixture is degassed by the repeated freeze/thaw procedure of Example E-1.

The prepolymer mixture is cured in a nitrogen atmosphere to form the contact lens. Subsequent to curing, the lens is plasma treated for about 7.5 minutes in an atmosphere of methane and air at a 2:1 CH₄:air volume ratio.

The Ionoton Ion Permeability Coefficient of the lens is 0.25×10^{-3} cm²/sec. Clinical examination shows that the lens moves on the human eye. See Table E for a summary of the results.

EXAMPLE E-9

Material C

A contact lens is prepared substantially in accordance with the procedure described in Example C-20. Prior to polymerization, the prepolymerization mixture is degassed by the repeated freeze/thaw procedure of Example E-1.

The prepolymer mixture is cured in an air atmosphere to form the contact lens. Subsequent to curing, the lens is not surface treated.

The Ionoton Ion Permeability Coefficient of the lens is 0.008×10^{-3} cm²/sec. Clinical examination shows that the lens does not move on the human eye. See Table E for a summary of the results.

EXAMPLE E-10

Material D

A contact lens is prepared substantially in accordance with the procedure described in Example D-2. Prior to polymerization, the prepolymerization mixture is degassed by the repeated freeze/thaw procedure of Example E-1.

The prepolymer mixture is cured in a nitrogen atmosphere to form the contact lens. Subsequent to curing, the lens is not surface treated.

64

The Ionoton Ion Permeability Coefficient of the lens is 1.4×10^{-3} cm²/sec. Clinical examination shows that the lens moves on the human eye. See Table E for a summary of the results.

EXAMPLE E-11

Material D

A contact lens is prepared substantially in accordance with the procedure described in Example D-2. Prior to polymerization, the prepolymerization mixture is degassed by the repeated freeze/thaw procedure of Example E-1.

The prepolymer mixture is cured in a nitrogen atmosphere to form the contact lens. Subsequent to curing, the lens is plasma treated for about 7.5 minutes in an atmosphere of methane and air at a 2:1 CH₄:air volume ratio.

The Ionoton Ion Permeability Coefficient of the lens is 0.61×10^{-3} cm²/sec. Clinical examination shows that the lens moves on the human eye. See Table E for a summary of the results.

EXAMPLE E-12

Material D

A contact lens is prepared substantially in accordance with the procedure described in Example D-2. Prior to polymerization, the prepolymerization mixture is degassed by the repeated freeze/thaw procedure of Example E-1.

The prepolymer mixture is cured in a nitrogen atmosphere to form the contact lens. Subsequent to curing, the lens is plasma treated for about 5 minutes in an atmosphere of methane and air at a 2:1 CH₄:air volume ratio.

The Ionoton Ion Permeability Coefficient of the lens is 1.5×10^{-3} cm²/sec. Clinical examination shows that the lens moves on the human eye. See Table E-I for a summary of the results.

EXAMPLE E-13

Material D

A contact lens is prepared substantially in accordance with the procedure described in Example D-2. Prior to polymerization, the prepolymerization mixture is degassed by the repeated freeze/thaw procedure of Example E-1.

The prepolymer mixture is cured in an air atmosphere to form the contact lens. Subsequent to curing, the lens is not surface treated.

The Ionoton Ion Permeability Coefficient of the lens is -0.001×10^{-3} cm²/sec. Clinical examination shows that the lens does not move on the human eye. See Table E for a summary of the results.

TABLE E

Example	Material	Degassing	Curing atmosphere	Surface treatment CH ₄ :air plasma [minutes]	Ionoton Ion Permeability Coefficient [10 ⁻³ cm ² /sec]	On-eye Movement
E-1	A	3-cycle freeze/thaw	nitrogen	10	0.81	YES
E-2	B	nitrogen bubble	nitrogen	no plasma	-0.063	NO

US 6,951,894 B1

65

66

TABLE E-continued

Example	Material	Degassing	Curing atmosphere	Surface treatment CH ₄ /air plasma [minutes]	Ionoton Ion Permeability Coefficient [10 ⁻³ cm ² /sec]	On-eye Movement
E-3	B	3-cycle freeze/thaw	nitrogen	3	0.50	YES
E-4	B	3-cycle freeze/thaw	nitrogen	5	0.47	YES
E-5	B	3-cycle freeze/thaw	nitrogen	7.5	0.35	YES
E-6	B	3-cycle freeze/thaw	nitrogen	no plasma	1.1	YES
E-7	C	3-cycle freeze/thaw	nitrogen	5	2.9	YES
E-8	C	3-cycle freeze/thaw	nitrogen	7.5	0.25	YES
E-9	C	3-cycle freeze/thaw	air	no plasma	0.008	NO
E-10	D	3-cycle freeze/thaw	nitrogen	no plasma	1.4	YES
E-11	D	3-cycle freeze/thaw	nitrogen	7.5	0.61	YES
E-12	D	3-cycle freeze/thaw	nitrogen	5	1.5	YES
E-13	D	3-cycle freeze/thaw	air	no plasma	-0.001	NO

Considering Examples E-1 through E-13 of Table E, the lowest value of Ionoton Ion Permeability Coefficient for which a lens moves on the eye is 0.25×10^{-3} cm²/sec. The highest value of Ionoton Ion Permeability Coefficient for a lens which bound on the eye is 0.008×10^{-3} cm²/sec. Thus, a contact lens preferably has an Ionoton Ion Permeability Coefficient greater than about 0.008×10^{-3} cm²/sec., more preferably greater than about 0.25×10^{-3} cm²/sec.

EXAMPLE F-1

Material C

A contact lens is prepared substantially in accordance with the procedure described in Example C-25. Prior to surface treatment, the Ionoflux Ion Permeability Coefficient is determined to be about 0 mm²/min.

Subsequent to ion permeability measurements, the lens surface is coated with polyvinylpyrrolidone (PVP) in accordance with the following procedure, using a glass plasma reactor equipped with an external ring electrode and a 27.13 MHz radio frequency (RF) generator for the generation of an inductively-coupled, cold glow discharge plasma. Highly purified argon is used as a plasma gas and as a carrier gas for N-vinylpyrrolidone (NVP) monomer feed. The NVP feed line is located about 10 cm below the glow zone.

The contact lens is placed in the 20 cm diameter plasma reactor at a position about 15 cm below the plasma glow zone. The reactor is then evacuated for about 30 minutes to about 0.009 mbar. Subsequent to evacuation, the plasma gas flow is set to 20 sccm (standard cubic centimeters), the glow discharge is started at a pressure of about 0.15 mbar and maintained for about one minute at a power of about 170 Watts (in order to clean and activate the lens surface). After reduction of argon plasma gas flow to about 10 sccm, the argon carrier gas flow for the NVP monomer is also set to 10 sccm. The temperature of the NVP source (with the carrier gas bubbling through the liquid NVP) is held at about 40° C. The lenses are treated for about 10 minutes with a pulsing glow discharge plasma (1 μ sec. on, 3 μ sec. off) at about 0.35 mbar pressure and about 150 Watts power.

After interrupting the glow discharge and the carrier gas flow, the reactor is continuously purged with a 20 sccm argon stream at a pressure of about 0.009 mbar for about 30 minutes, in order to remove residual monomer and activated species. The PVP coated contact lenses thus produced are highly wettable and show the following contact dynamic contact angles, measured with a KRUESS (Hamburg, Germany) K-12 instrument:

	Untreated	Treated
Advancing	102	38
Receding	48	23
Hysteresis	53	15

Clinical tests show that the lens does not move on the eye. See Table F for a summary of the results.

EXAMPLE F-2

Material C

A contact lens is prepared substantially in accordance with the procedure described in Example C-26. Prior to surface treatment, the Ionoflux Ion Permeability Coefficient is determined to be about 2.8×10^{-7} mm²/min.

Subsequent to ion permeability measurements, the lens surface is coated with polyvinylpyrrolidone as in Example F-1. Clinical tests show that the lens does not move on the eye. See Table F for a summary of the results.

EXAMPLE F-3

Material C

A contact lens is prepared substantially in accordance with the procedure described in Example C-27. Prior to surface treatment, the Ionoflux Ion Permeability Coefficient is determined to be about 9.3×10^{-7} mm²/min.

Subsequent to ion permeability measurements, the lens surface is coated with polyvinylpyrrolidone as in Example

US 6,951,894 B1

67

F-1. Clinical tests show that the lens does not move on the eye. See Table F for a summary of the results.

EXAMPLE F-4**Material C**

A contact lens is prepared substantially in accordance with the procedure described in Example C-18. Prior to surface treatment, the Ionoflux Ion Permeability Coefficient is determined to be about 2.6×10^{-6} mm²/min.

Subsequent to ion permeability measurements, the lens surface is coated with polyvinylpyrrolidone as in Example F-1. Clinical tests show that the lens moves on the eye. See Table F for a summary of the results.

EXAMPLE F-5**Material C**

A contact lens is prepared substantially in accordance with the procedure described in Example C-16. Prior to surface treatment, the Ionoflux Ion Permeability Coefficient is determined to be about 1.3×10^{-5} mm²/min.

Subsequent to ion permeability measurements, the lens surface is coated with polyvinylpyrrolidone as in Example F-1. Clinical tests show that the lens moves on the eye. See Table F for a summary of the results.

EXAMPLE F-6**Material C**

A contact lens is prepared substantially in accordance with the procedure described in Example C-19. Prior to surface treatment, the Ionoflux Ion Permeability Coefficient is determined to be about 2.7×10^{-5} mm²/min.

Subsequent to ion permeability measurements, the lens surface is coated with polyvinylpyrrolidone as in Example F-1. Clinical tests show that the lens moves on the eye. See Table F for a summary of the results.

EXAMPLE F-7**Material C**

A contact lens is prepared substantially in accordance with the procedure described in Example C-17. Prior to surface treatment, the Ionoflux Ion Permeability Coefficient is determined to be about 7.8×10^{-6} mm²/min.

Subsequent to ion permeability measurements, the lens surface is coated with polyvinylpyrrolidone as in Example F-1. Clinical tests show that the lens moves on the eye. See Table F for a summary of the results.

EXAMPLE F-8**Material B**

A contact lens is prepared substantially in accordance with the procedure described in Example B-13. Prior to surface treatment, the Ionoflux Ion Permeability Coefficient is determined to be about 1.5×10^{-6} mm²/min.

Subsequent to ion permeability measurements, the lens surface is coated with polyvinylpyrrolidone as in Example F-1. Clinical tests show that the lens does not move on the eye. See Table F for a summary of the results.

EXAMPLE F-9**Material B**

A contact lens is prepared substantially in accordance with the procedure described in Example B-14. Prior to

68

surface treatment, the Ionoflux Ion Permeability Coefficient is determined to be about 1.1×10^{-3} mm²/min.

Subsequent to ion permeability measurements, the lens surface is coated with polyvinylpyrrolidone as in Example F-1. Clinical tests show that the lens does not move on the eye. See Table F for a summary of the results.

EXAMPLE F-10**Material B**

A contact lens is prepared substantially in accordance with the procedure described in Example B-7. Prior to surface treatment, the Ionoflux Ion Permeability Coefficient is determined to be about 3.8×10^{-6} mm²/min.

Subsequent to ion permeability measurements, the lens surface is coated with polyvinylpyrrolidone as in Example F-1. Clinical tests show that the lens moves on the eye. See Table F for a summary of the results.

EXAMPLE F-11**Material B**

A contact lens is prepared substantially in accordance with the procedure described in Example B-6. Prior to surface treatment, the Ionoflux Ion Permeability Coefficient is determined to be about 8.5×10^{-6} mm²/min.

Subsequent to ion permeability measurements, the lens surface is coated with polyvinylpyrrolidone as in Example F-1. Clinical tests show that the lens moves on the eye. See Table F for a summary of the results.

EXAMPLE F-12**Material B**

A contact lens is prepared substantially in accordance with the procedure described in Example B-5. Prior to surface treatment, the Ionoflux Ion Permeability Coefficient is determined to be about 7.1×10^{-5} mm²/min.

Subsequent to ion permeability measurements, the lens surface is coated with polyvinylpyrrolidone as in Example F-1. Clinical tests show that the lens moves on the eye. See Table F for a summary of the results.

TABLE F

EX- AMPLE	MATERIAL (Example reference number)	IONOFLUX ION PERMEABILITY COEFFICIENT* [mm ² /min]	ON-EYE MOVEMENT- CLINICAL DETERMINATION
F-1	C-25	0	NO
F-2	C-26	0.28×10^{-6}	NO
F-3	C-27	0.93×10^{-6}	NO
F-4	C-18	2.6×10^{-6}	YES
F-5	C-16	13.0×10^{-6}	YES
F-6	C-19	27.0×10^{-6}	YES
F-7	C-17	7.8×10^{-6}	YES
F-8	B-13	1.5×10^{-6}	NO
F-9	B-14	1.1×10^{-6}	NO
F-10	B-7	3.8×10^{-6}	YES
F-11	B-6	8.5×10^{-6}	YES
F-12	B-5	71.0×10^{-6}	YES

*All Ionoflux Ion Permeability Coefficients were determined on uncoated lenses.

Considering only Examples F-1 through F-13 of Table F, the lowest value of Ionoflux Ion Permeability Coefficient for which a lens moves on the eye is 2.6×10^{-6} mm²/min. The highest value of Ionoflux Ion Permeability Coefficient for a

US 6,951,894 B1

69

lens which binds on the eye is 1.5×10^{-6} mm²/min. Thus, a contact lens preferably has an Ionoflux Ion Permeability Coefficient greater than about 1.5×10^{-6} mm²/min., more preferably greater than about 2.6×10^{-6} mm²/min.

EXAMPLE G-1

A contact lens is prepared substantially in accordance with the procedure described in Example A-2. The Hydrodell Water Permeability Coefficient is determined to be about 0.71×10^{-6} cm²/second. Clinical tests show that the lens moves on the eye. See Table G for a summary of the results.

EXAMPLE G-2

A contact lens is prepared substantially in accordance with the procedure described in Example B-5. The Hydrodell Water Permeability Coefficient is determined to be about 1.09×10^{-6} cm²/second. Clinical tests show that the lens moves on the eye. See Table G for a summary of the results.

EXAMPLE G-3

A contact lens is prepared substantially in accordance with the procedure described in Example B-6. The lens is surface treated in a plasma gas in accordance with the procedure described in Example F-1. The Hydrodell Water Permeability Coefficient is determined to be about 0.27×10^{-6} cm²/second. Clinical tests show that the lens moves on the eye. See Table G for a summary of the results.

EXAMPLE G-4

A contact lens is prepared substantially in accordance with the procedure described in Example C-19. The lens is surface treated in a plasma gas in accordance with the procedure described in Example F-1. The Hydrodell Water Permeability Coefficient is determined to be about 0.37×10^{-6} cm²/second. Clinical tests show that the lens moves on the eye. See Table G for a summary of the results.

EXAMPLE G-5

A contact lens is prepared substantially in accordance with the procedure described in Example D-2. The Hydrodell Water Permeability Coefficient is determined to be about 1.26×10^{-6} cm²/second. Clinical tests show that the lens moves on the eye. See Table G for a summary of the results.

EXAMPLE G-6

A contact lens is prepared substantially in accordance with the procedure described in Example C-14. The Hydrodell Water Permeability Coefficient is determined to be about 0.08×10^{-6} cm²/second. Clinical tests show that the lens does not move on the eye. See Table G for a summary of the results.

TABLE G

EX- AMPLE	MA- TERIAL (Example reference number)	SUR- FACE TREAT- MENT	HYDRODELL WATER PERMEABILITY COEFFICIENT [cm ² /sec.]	ON-EYE MOVEMENT- CLINICAL DETERMINATION
G-1	A-2	none	0.71×10^{-6}	YES
G-2	B-5	none	1.09×10^{-6}	YES
G-3	B-6	PVP	0.27×10^{-6}	YES
G-4	C-19	PVP	0.37×10^{-6}	YES

70

TABLE G-continued

EX- AMPLE	MA- TERIAL (Example reference number)	SUR- FACE TREAT- MENT	HYDRODELL WATER PERMEABILITY COEFFICIENT [cm ² /sec.]	ON-EYE MOVEMENT- CLINICAL DETERMINATION
G-5	D-2	none	1.26×10^{-6}	YES
G-6	C-14	none	0.08×10^{-6}	NO

Considering only Examples G-1 through G-6 of Table G, the lowest value of Hydrodell Water Permeability Coefficient for which a lens moves on the eye is 0.27×10^{-6} cm²/sec. The highest value of Hydrodell Water Permeability Coefficient for a lens which binds on the eye is 0.08×10^{-6} cm²/sec. Thus, a contact lens preferably has a Hydrodell Water Permeability Coefficient greater than about 0.08×10^{-6} cm²/sec., more preferably greater than 0.27×10^{-6} cm²/sec.

The invention has been described in detail, with reference to certain preferred embodiments, in order to enable the reader to practice the invention without undue experimentation. Theories of operation have been offered to better enable the reader to understand the invention, but such theories do not limit the scope of the invention. In addition, a person having ordinary skill in the art will readily recognize that many of the previous components, compositions, and parameters may be varied or modified to a reasonable extent without departing from the scope and spirit of the invention. Furthermore, titles, headings, example materials or the like are provided to enhance the reader's comprehension of this document, and should not be read as limiting the scope of the present invention. Accordingly, the intellectual property rights to the invention are defined by the following claims, reasonable extensions and equivalents thereof, as interpreted in view of the disclosure herein.

That which is claimed is:

1. A method for producing an extended wear contact lens, said contact lens comprising a core polymeric material which has a high oxygen permeability and a high ion or water permeability, which method comprises the steps of:

- preparing a lens formulation comprising an oxyperm polymerizable material selected from the group consisting of fluorine-containing macromers and fluorine-containing monomers, and an ionoperm polymerizable material selected from the group consisting of acrylates, methacrylates, polyalkylene glycols and N-vinyl pyrrolidones, wherein said oxyperm polymerizable material comprises between about 30% to about 70%, based on the total weight, of said lens formulation;
- placing said lens formulation in a lens mold;
- polymerizing- said lens formulation in said mold to form a lens core material having inner and outer surfaces such that said oxyperm polymerizable material and said ionoperm polymerizable material of said lens formulation form separate oxyperm and ionoperm phases; said lens core material having an oxygen permeability equal to or greater than 77 barrers;
- removing said lens core material from said lens mold;
- subjecting said lens core material to a treatment to modify said surfaces of said lens core material, wherein the surface treatment makes said surfaces more biocompatible with the ocular tissue and ocular fluids than said core material alone; and

US 6,951,894 B1

71

f) hydrating the treated lens core material to produce a hydrated extended wear contact lens,

wherein the modified surfaces of said lens in conjunction with the high oxygen and ion permeabilities of said core polymeric material allows said hydrated lens to be worn as extended wear lens that is worn for a continuous period of at least 24 hours with corneal swelling of less than about 8%.

2. The method of claim 1 wherein the surface modification treatment is selected from the group consisting of coating processes, grafting processes, plasma treating processes, electrical charge treating processes and irradiation processes.

3. The method of claim 1 wherein the surface modification treatment is a plasma treating process.

4. The method of claim 3 wherein said oxyperm polymerizable material is a fluorine-containing macromer and said ionoperm polymerizable material is N-vinyl pyrrolidone.

5. An extended wear contact lens comprising a core polymeric material and upper and lower surfaces, said core polymeric material comprising a silicone copolymer which provides a high ion permeability and a high oxygen permeability; wherein said silicone copolymer comprises an oxyperm polymerizable material selected from the group consisting of fluorine-containing macromers and fluorine-containing monomers, and an ionoperm polymerizable material selected from the group consisting of acrylates, methacrylates, polyalkylene glycols and N-vinyl pyrrolidones; said core polymeric material having an oxygen permeability equal to or greater than 77 barrers; wherein said surfaces are hydrophilically modified by a treatment process selected from the group consisting of coating processes, grafting processes, plasma treating processes, electrical charge treating processes and irradiation processes; and wherein said extended wear contact lens can be continuously worn for at least four days on a human eye without substantial corneal swelling.

6. The extended contact lens of claim 5 wherein said core polymeric material comprises a fluorine containing macromer, and N-vinyl pyrrolidone.

7. The extended contact lens of claim 6 wherein said surfaces are modified by a plasma treating process.

8. The extended contact lens of claim 7 wherein said extended lens can be continuously worn for about 7 days with less than about 8% corneal swelling.

9. The extended contact lens of claim 5 wherein said wended lens is worn for about 30 days.

10. A hydrogel contact lens having modified surfaces, said hydrogel contact lens comprising a core polymeric material having an oxygen permeability equal to or greater than 77 barrers, said hydrogel contact lens being suited to make contact with ocular tissue and ocular fluids and having a high oxygen permeability and a high ion permeability, said core polymeric material having formed from polymerizable materials comprising:

(a) an oxyperm polymerizable material selected from the group consisting of fluorine-containing macromers and fluorine-containing monomers, and

(b) an ionoperm polymerizable material selected from the group consisting of acrylates, methacrylates, polyalkylene glycols and N-vinyl pyrrolidones,

wherein said lens has a high oxygen permeability and allows ion or water permeation in an amount sufficient to enable the lens to move on the eye such that corneal health is not substantially harmed and wearer comfort is acceptable during a period of continuous contact with

72

ocular tissue and ocular fluids, wherein said lens has an oxygen permeability of at least about 77 barrers and an ion permeability characterized either by an Ionoflux Ion Diffusion Coefficient of greater than about 6.4×10^{-6} mm²/sec or an Ionoton Ion Permeability Coefficient of greater than about 0.4×10^{-6} cm²/min,

wherein said modified surfaces are hydrophilically modified surfaces that are modified by a treatment process selected from the group consisting of coating processes, grafting processes, plasma treating processes, electrical charge treating processes and irradiation processes,

wherein said hydrogel contact lens is adapted for at least 24 hours of continuous wear on a human eye without substantial corneal swelling.

11. The hydrogel contact lens of claim 10 wherein said core polymeric material comprises a fluorine containing macromer as said oxyperm material and N-vinyl pyrrolidone as said ionoperm material.

12. The hydrogel contact lens of claim 11 wherein said surfaces are modified by a plasma treating process.

13. The hydrogel contact lens of claim 12 wherein said lens can be worn for about 7 days with less than about 8% corneal swelling.

14. The hydrogel contact lens of claim 12 wherein said lens is worn for about 7 days with less than about 4% corneal swelling.

15. The hydrogel contact lens of claim 12 wherein said lens can be continuously worn for about 30 days.

16. The hydrogel contact lens of claim 12 wherein said lens has an oxygen permeability of at least about 81 barrers.

17. A method of using a contact lens as an extended wear lens, said lens having ophthalmically compatible modified surfaces, said lens being suited to extended periods of wear in continuous, intimate contact with ocular tissue and ocular fluids, said lens comprising a polymeric material which has a high oxygen permeability and a high ion or water permeability, and which has an oxygen permeability equal to or greater than 77 barrers, said polymeric material being formed from polymerizable materials comprising:

(a) an oxyperm polymerizable material selected from the group consisting of fluorine-containing macromers and fluorine-containing monomers, and

(b) an ionoperm polymerizable material selected from the group consisting of acrylates, methacrylates, polyalkylene glycols and N-vinyl pyrrolidones,

wherein said modified surfaces are modified by a treatment process selected from the group consisting of coating processes, grafting processes, plasma treating processes, electrical charge treating processes and irradiation processes;

wherein said lens allows oxygen permeation in an amount sufficient to maintain corneal health and wearer comfort during a period of extended, continuous contact with ocular tissue and ocular fluids;

wherein said lens allows ion or water permeation in an amount sufficient to enable the lens to move on the eye such that corneal health is not substantially harmed and wearer comfort is acceptable during a period of extended, continuous contact with ocular tissue and ocular fluids; and

wherein said ophthalmic lens has an oxygen permeability of at least about 70 barrers and an ion permeability characterized either by (1) an Ionoton Ion Permeability Coefficient of greater than about 0.4×10^{-6} cm²/sec or (2) an Ionoflux Diffusion Coefficient of greater than

US 6,951,894 B1

73

about 6.4×10^{-6} mm²/min, wherein said ion permeability is measured with respect to sodium ions;

said method comprising the steps of:

- (a) applying said lens to the ocular environment, and
- (b) allowing said lens to remain in intimate contact with the ocular environment for a period of at least 24 hours.

18. The method of claim 17 wherein said lens has an oxygen permeability of at least about 81 barrers.

19. The method of claim 17 wherein said intimate contact period is at least 4 days.

20. The method of claim 17 wherein said intimate contact period is about 7 days.

21. The method of claim 17 wherein said intimate contact period is about 14 days.

22. The method of claim 17 wherein said intimate contact period is about 30 days.

23. The method of claim 17 wherein said lens produces, after wear of about 24 hours, including normal steep periods, less than about 8% corneal swelling.

24. The method of claim 17 wherein said lens produces, after wear of about 7 days, including normal sleep periods, less than about 6% corneal swelling.

25. A method for producing an extended wear contact lens, said contact lens comprising a core polymeric material which has a high oxygen permeability and a high ion or water permeability, which method comprises the steps of:

- a) preparing a lens formulation comprising an oxypolymerizable material, and an ionopolymerizable material, wherein said oxypolymerizable material comprises between about 30% to about 70%, based on the total weight, of said lens formulation;
- b) placing said lens formulation in a lens mold;
- c) polymerizing said lens formulation in said mold to form a lens core material having inner and outer surfaces such that said oxypolymerizable material and said ionopolymerizable material of said lens formulation form separate oxypolymer and ionopolymer phases; said lens core material having an oxygen permeability equal to or greater than 69 barrers;
- d) removing said lens core material from said lens mold;
- e) subjecting said lens core material to a treatment to modify said surfaces of said lens core material, wherein the surface treatment makes said surfaces more hydrophilic or lipophobic and more biocompatible with the ocular tissue than said core material alone; and
- f) hydrating the treated lens core material to produce a hydrated extended wear contact lens,

wherein the modified surfaces of said lens in conjunction with the high oxygen and ion permeabilities of said core polymeric material allows said hydrated lens to be worn as extended wear lens that is worn for a continuous period of at least 24 hours without having substantial amounts of lipid adsorption.

26. The method of claim 25 wherein the surface modification treatment is selected from the group consisting of coating processes, grafting processes, plasma treating processes, electrical charge treating processes and irradiation processes.

27. The method of claim 25 wherein the surface modification treatment is a plasma treating process.

28. The method of claim 27 wherein said oxypolymerizable material is a fluorine macromer and said ionopolymerizable material is N-vinyl pyrrolidone.

29. An extended wear contact lens comprising a core polymeric material and upper and lower surfaces, said core

74

polymeric material comprising a silicone copolymer which provides a high ion permeability and a high oxygen permeability; said silicone copolymer comprising an oxypolymerizable material, and an ionopolymerizable material; said core polymeric material having an oxygen permeability equal to or greater than 69 barrers; wherein said surfaces are hydrophilically modified by a treatment process selected from the group consisting of coating processes, grafting processes, plasma treating processes, electrical charge treating processes and irradiation processes; and wherein said extended wear contact lens can be continuously worn for at least four days on a human eye without substantial corneal swelling and without having substantial amounts of lipid adsorption.

30. The extended contact lens of claim 29 wherein said core polymeric material comprises a fluorine macromer, and N-vinyl pyrrolidone.

31. The extended contact lens of claim 30 wherein said surfaces are modified by a plasma treating process.

32. The extended contact lens of claim 31 wherein said extended lens can be continuously worn for about 7 days with less than about 7% corneal swelling.

33. The extended contact lens of claim 29 wherein said extended wear lens can be worn for about 30 days.

34. A siloxane hydrogel contact lens having modified surfaces, said hydrogel contact lens comprising a core polymeric material having an oxygen permeability equal to or greater than 69 barrers, said hydrogel contact lens being suited to make contact with ocular tissue and ocular fluids and having a high oxygen permeability and a high ion permeability, said core polymeric material being formed from polymerizable materials comprising:

- (a) an oxypolymerizable material, and
- (b) an ionopolymerizable material, wherein said lens has a high oxygen permeability and allows ion or water permeation in an amount sufficient to enable the lens to move on the eye such that corneal health is not substantially harmed and wearer comfort is acceptable during a period of continuous contact with ocular tissue and ocular fluids, wherein said lens has an oxygen permeability of at least about 69 barrers and an ion permeability characterized either by an Ionoflux Ion Diffusion Coefficient of greater than about 6.4×10^{-6} mm²/sec or an Ionoton Ion Permeability Coefficient of greater than about 0.4×10^{-6} cm²/min,

wherein said modified surfaces are hydrophilically modified surfaces that are modified by a treatment process selected from the group consisting of coating processes, grafting processes, plasma treating processes, electrical charge treating processes and irradiation processes,

wherein said hydrogel contact lens is adapted for at least 24 hours of continuous wear on a human eye without substantial corneal swelling and without having substantial amounts of lipid adsorption.

35. The hydrogel contact lens of claim 34 wherein said core polymeric material comprises a fluorine containing macromer as said oxypolymerizable material and N-vinyl pyrrolidone as said ionopolymerizable material.

36. The hydrogel contact lens of claim 35 wherein said surfaces are modified by a plasma treating process.

37. The hydrogel contact lens of claim 36 wherein said lens can be worn for about 7 days in continuous contact with ocular tissues and fluids with less than about 8% corneal swelling.

38. The hydrogel contact lens of claim 36 wherein said lens is worn for about 7 days with less than about 4% corneal swelling.

US 6,951,894 B1

75

39. The hydrogel contact lens of claim 36 wherein said lens can be continuously worn for about 30 days.

40. The hydrogel contact lens of claim 36 wherein said lens has an oxygen permeability of at least about 77 barrers.

41. A method of using a contact lens as an extended wear lens, said lens having ophthalmically compatible modified surfaces, said lens being suited to extended periods of wear in continuous, intimate contact with ocular tissue and ocular fluids, said lens comprising a polymeric material which has a high oxygen permeability and a high ion or water permeability, and which has an oxygen permeability equal to or greater than 69 barrers, said polymeric material being formed from polymerizable materials comprising:

- (a) an oxyperm polymerizable material, and
- (b) an ionoperm polymerizable material,

wherein said modified surfaces are modified by a treatment process selected from the group consisting of coating processes, grafting processes, plasma treating processes, electrical charge treating processes and irradiation processes;

wherein said lens allows oxygen permeation in an amount sufficient to maintain corneal health and wearer comfort during a period of extended, continuous contact with ocular tissue and ocular fluids;

wherein said lens allows ion or water permeation in an amount sufficient to enable the lens to move on the eye such that corneal health is not substantially harmed and wearer comfort is acceptable during a period of extended, continuous contact with ocular tissue and ocular fluids without having substantial amounts of lipid adsorption; and

wherein said ophthalmic lens has an oxygen permeability of at least about 70 barrers and an ion permeability characterized either by (1) an Ionoton Ion Permeability Coefficient of greater than about $0.4 \times 10^{-6} \text{ cm}^2/\text{sec}$ or (2) an Ionoflux Diffusion Coefficient of greater than about $6.4 \times 10^{-6} \text{ mm}^2/\text{min}$, wherein said ion permeability is measured with respect to sodium ions;

said method comprising the steps of:

- (a) applying said lens to the ocular environment, and
- (b) allowing said lens to remain in continuous intimate contact with the ocular environment for a period of at least 24 hours without having substantial amounts of lipid adsorption.

42. The method of claim 41 wherein said lens has an oxygen permeability of at least about 77 barrers.

43. The method of claim 41 wherein said intimate contact period is at least 4 days.

44. The method of claim 41 wherein said intimate contact period is about 7 days.

45. The method of claim 41 wherein said intimate contact period is about 14 days.

46. The method of claim 41 wherein said intimate contact period is about 30 days.

47. The method of claim 41 wherein said lens produces, after wear of about 24 hours, including normal steep periods, less than about 8% corneal swelling.

48. The method of claim 41, wherein said lens produces, after wear of about 7 days, including normal sleep periods, less than about 6% corneal swelling.

49. A method of forming a biocompatible lens having high oxygen permeability and high water permeability, said method comprising the steps of:

- (a) forming a polymeric core formulation comprising an oxyperm polymerizable material, and an ionoperm polymerizable material, said oxyperm polymerizable

76

material comprises between about 30% to about 70%, based on the total weight, of said lens formulation;

(b) polymerizing the core in an atmosphere substantially free from oxygen;

(c) altering the surface of said core material to produce a surface which is more hydrophilic than said core material; and

(d) autoclaving lens at predetermined temperatures;

whereby said lens allows oxygen permeation in an amount sufficient to maintain corneal health and wearer comfort during a period of extended, continuous contact with ocular tissue and ocular fluids, and

whereby said lens allows ion permeation in an amount sufficient to enable the lens to move on the eye such that corneal health is not substantially harmed and wearer comfort is acceptable during a period of extended, continuous contact with ocular tissue and ocular fluids,

wherein said lens having adequate movement on the eye with blinking to promote adequate tear exchange and without producing significant corneal swelling, without having substantial amounts of lipid adsorption, and without causing substantial wearer discomfort during the period of contact for at least 24 hours,

wherein said ophthalmic lens has an oxygen transmissibility of at least about 70 barrers/mm and an ion permeability characterized either by (1) an Ionoton Ion Permeability Coefficient of greater than about $0.2 \times 10^{-6} \text{ cm}^2/\text{sec}$ or (2) by an Ionoflux Ion Permeability Coefficient of greater than about $1.5 \times 10^{-6} \text{ mm}^2/\text{min}$, wherein said ion permeability is measured with respect to sodium ions.

50. A method of forming a contact lens having high oxygen permeability and high water permeability, said method comprising:

(a) forming a polymeric core material in the shape of a contact lens having an inner and outer surface; and

(b) altering the surfaces of said core material to produce new surfaces that are more hydrophilic than said core material,

wherein said lens having adequate movement on the eye with blinking to promote adequate tear exchange and without producing significant corneal swelling, without having substantial amounts of lipid adsorption, and without causing substantial wearer discomfort during the period of contact for at least 24 hours.

51. The method of claim 50 wherein said intimate contact period is about 7 days.

52. The method of claim 50 wherein said intimate contact period is about 30 days.

53. The method of claim 50 wherein said lens is autoclaved at predetermined temperatures.

54. A biocompatible contact lens having high oxygen permeability and high water permeability, said lens comprising:

(a) a polymeric core material in the shape of a contact lens having an inner and outer surface; and

(b) said surfaces of said core material being surface modified to produce new surfaces that are more hydrophilic than said core material,

wherein said lens having adequate movement on the eye with blinking to promote adequate tear exchange and without producing significant corneal swelling, without having substantial amounts of lipid adsorption, and without causing substantial wearer discomfort during the period of contact for at least 24 hours.

US 6,951,894 B1

77

55. The lens of claim 54 wherein said intimate contact period is at least 4 days.

56. The lens of claim 55 wherein said intimate contact period is about 7 days.

57. The lens of claim 55 wherein said intimate contact period is about 14 days.

58. The lens of claim 55 wherein said intimate contact period is about 30 days.

59. The lens of claim 54 including (c) said said lens being autoclaved at predetermined temperatures.

60. A method for producing an extended wear contact lens, said contact lens comprising a core polymeric material which has a high oxygen permeability and a high ion or water permeability, which method comprises the steps of:

a) preparing a lens formulation comprising an oxyperm polymerizable material, and an ionoperm polymerizable material, wherein said oxyperm polymerizable material comprises between about 30% to about 70%, based on the total weight, of said lens formulation;

b) placing said lens formulation in a lens mold;

c) polymerizing said lens formulation in said mold to form a lens core material having inner and outer surfaces such that said oxyperm polymerizable material and said ionoperm polymerizable material of said lens formulation form separate oxyperm and ionoperm phases; said lens core material having an oxygen permeability equal to or greater than 69 barrers;

d) removing said lens core material from said lens mold;

e) subjecting said lens core material to a treatment to modify said surfaces of said lens core material, wherein the surface treatment makes said surfaces more hydrophilic or lipophobic and more biocompatible with the ocular tissue than said core material alone; and

f) hydrating the treated lens core material to produce a hydrated extended wear contact lens,

wherein the modified surfaces of said lens in conjunction with the high oxygen and ion permeabilities of said core polymeric material allows said hydrated lens to be worn as extended wear lens that is worn for a continuous period of at least 24 hours without having substantial amounts of lipid adsorption.

61. A method for producing an extended wear contact lens, said contact lens comprising a core polymeric material which has a high oxygen permeability and a high ion or water permeability, which method comprises the steps of:

a) preparing a lens formulation comprising an oxyperm polymerizable material selected from the group consisting of siloxane-containing macromers, fluorine-containing macromers and fluorine monomers, and an ionoperm polymerizable material, wherein said oxyperm polymerizable material comprises between about 30% to about 70%, based on the total weight, of said lens formulation;

b) placing said lens formulation in a lens mold;

c) polymerizing said lens formulation in said mold to form a lens core material having inner and outer surfaces such that said oxyperm polymerizable material and said ionoperm polymerizable material of said lens formulation form separate oxyperm and ionoperm phases; said lens core material having at least one continuous pathway from said inner surface to said outer surface for oxygen transmission therethrough;

d) removing said lens core material from said lens mold;

e) subjecting said lens core material to a treatment to modify said surfaces of said lens core material, wherein

78

the surface treatment makes said surfaces more hydrophilic or lipophobic and more biocompatible with the ocular tissue than said core material alone; and

f) hydrating the treated lens core material to produce a hydrated extended wear contact lens,

wherein the modified surfaces of said lens in conjunction with the high oxygen and ion permeabilities of said core polymeric material allows said hydrated lens to be worn as extended wear lens that is worn for a continuous period of at least 24 hours with corneal swelling of less than about 8%.

62. The method of claim 61 wherein the surface modification treatment is selected from the group consisting of coating processes, grafting processes, plasma treating processes, electrical charge treating processes and irradiation processes.

63. The method of claim 61 wherein the surface modification treatment is a plasma treating process.

64. The method of claim 63 wherein said oxyperm polymerizable material is a siloxane containing macromer or siloxane containing monomer and said ionoperm polymerizable material is N-vinyl pyrrolidone.

65. An extended wear contact lens comprising a core polymeric material and upper and lower surfaces, said core polymeric material comprising a silicone copolymer which provides a high ion permeability and a high oxygen permeability; wherein said silicone copolymer comprises an oxyperm polymerizable material selected from the group consisting of siloxane-containing macromers, siloxane-containing monomers, fluorine-containing macromers, siloxane containing monomers and fluorine-containing monomers, and an ionoperm polymerizable material selected from the group consisting of acrylates, methacrylates, polyalkylene glycols and N-vinyl pyrrolidones, wherein said core polymeric material has at least one continuous pathway from said upper surface to said lower surface for oxygen transmission;

wherein said surfaces are hydrophilically modified by a treatment process selected from the group consisting of coating processes, grafting processes, plasma treating processes, electrical charge treating processes and irradiation processes; and wherein said extended wear contact lens can be continuously worn for at least four days on a human eye without substantial corneal swelling.

66. The extended contact lens of claim 65 wherein said core polymeric material comprises a siloxane-containing macromer or a siloxane monomer, and N-vinyl pyrrolidone.

67. The extended contact lens of claim 66 wherein said surfaces are modified by a plasma treating process.

68. The extended contact lens of claim 67 wherein said extended lens can be continuously worn for about 7 days with less than about 8% corneal swelling.

69. The extended contact lens of claim 66 wherein said extended wear lens can be worn for about 30 days.

70. A hydrogel contact lens having modified surfaces, said hydrogel contact lens comprising a core polymeric material having at least one continuous pathway between said surfaces for oxygen transmission therethrough, said hydrogel contact lens being suited to make contact with ocular tissue and ocular fluids and having a high oxygen permeability and a high ion permeability, said core polymeric material having formed from polymerizable materials comprising:

(a) an oxyperm polymerizable material selected from the group consisting of siloxane-containing macromers, siloxane-containing monomers, fluorine-containing macromers and fluorine-containing monomers, and

US 6,951,894 B1

79

(b) an ionoperm polymerizable material selected from the group consisting of acrylates, methacrylates, polyalkylene glycols and N-vinyl pyrrolidones,

wherein said lens has a high oxygen permeability and allows ion or water permeation in an amount sufficient to enable the lens to move on the eye such that corneal health is not substantially harmed and wearer comfort is acceptable during a period of continuous contact with ocular tissue and ocular fluids, wherein said lens has an oxygen permeability of at least about 70 barrers and an ion permeability characterized either by an Ionoflux Ion Diffusion Coefficient of greater than about 6.4×10^{-6} mm²/sec or an Ionoton Ion Permeability Coefficient of greater than about 0.4×10^{-6} cm²/min,

wherein said modified surfaces are hydrophilically modified surfaces that are modified by a treatment process selected from the group consisting of coating processes, grafting processes, plasma treating processes, electrical charge treating processes and irradiation processes,

wherein said hydrogel contact lens is adapted for at least 24 hours of continuous wear on a human eye without substantial corneal swelling.

71. The hydrogel contact lens of claim 70 wherein said core polymeric material comprises a siloxane-containing macromer or a siloxane containing monomer as said oxyperm material and N-vinyl pyrrolidone as said ionoperm material.

72. The hydrogel contact lens of claim 71 wherein said surfaces are modified by a plasma treating process.

73. The hydrogel contact lens of claim 72 wherein said lens can be worn for about 7 days with less than about 8% corneal swelling.

74. The hydrogel contact lens of claim 72 wherein said lens is worn for about 7 days with less than about 4% corneal swelling.

75. The hydrogel contact lens of claim 72 wherein said lens can be continuously worn for about 30 days.

76. The hydrogel contact lens of claim 72 wherein said lens has an oxygen permeability of at least 75 days.

77. A method of using a contact lens as an extended wear lens, said lens having ophthalmically compatible modified surfaces, said lens being suited to extended periods of wear in continuous, intimate contact with ocular tissue and ocular fluids, said lens comprising a polymeric material which has a high oxygen permeability and a high ion or water permeability, and which has at least one continuous pathway between said modified surfaces for oxygen surfaces, said polymeric material being formed from polymerizable materials comprising:

80

(a) an oxyperm polymerizable material, and

(b) an ionoperm polymerizable material,

wherein said modified surfaces are modified by a treatment process selected from the group consisting of coating processes, grafting processes, plasma treating processes, electrical charge treating processes and irradiation processes;

wherein said lens allows oxygen permeation in an amount sufficient to maintain corneal health and wearer comfort during a period of extended, continuous contact with ocular tissue and ocular fluids;

wherein said lens allows ion or water permeation in an amount sufficient to enable the lens to move on the eye such that corneal health is not substantially harmed and wearer comfort is acceptable during a period of extended, continuous contact with ocular tissue and ocular fluids without having substantial amounts of lipid absorption; and

wherein said ophthalmic lens has an oxygen permeability of at least about 70 barrers and an ion permeability characterized either by (1) an Ionoton Ion Permeability Coefficient of greater than about 0.4×10^{-6} cm²/sec or (2) an Ionoflux Diffusion Coefficient of greater than about 6.4×10^{-6} mm²/min, wherein said ion permeability is measured with respect to sodium ions;

said method comprising the steps of:

(a) applying said lens to the ocular environment, and
(b) allowing said lens to remain in continuous intimate contact with the ocular environment for a period of at least 24 hours.

78. The method of claim 77 wherein said lens has an oxygen permeability of at least about 77 barrers.

79. The method of claim 77 wherein said intimate contact period is at least 4 days.

80. The method of claim 77 wherein said intimate contact period is about 7 days.

81. The method of claim 77 wherein said intimate contact period is about 14 days.

82. The method of claim 77 wherein said intimate contact period is about 30 days.

83. The method of claim 77, wherein said lens produces, after wear of about 24 hours, including normal steep periods, less than about 8% corneal swelling.

84. The method of claim 77, wherein said lens produces, after wear of about 7 days, including normal sleep periods, less than about 6% corneal swelling.

* * * * *

UNITED STATES PATENT AND TRADEMARK OFFICE
CERTIFICATE OF CORRECTION

PATENT NO. : 6,951,894 B1
DATED : October 4, 2005
INVENTOR(S) : Nicolson et al.

Page 1 of 4

It is certified that error appears in the above-identified patent and that said Letters Patent is hereby corrected as shown below:

Column 70,

Line 55, change "polymerizing-said" to -- polymerizing said --.

Column 71,

Line 21, change "material and upper" to -- material having upper --.

Column 72,

Line 4, change "of grater than" to -- of greater than --.

Line 4, change " 6.4×10^{-6} " to -- 6.4×10^{-6} --.

Lines 6 and 65, change " 0.4×10^{-6} " to -- 0.4×10^{-6} --.

Column 73,

Line 1, change " 6.4×10^{-6} " to -- 6.4×10^{-6} --.

Column 74,

Line 43, change " 6.4×10^{-6} " to -- 6.4×10^{-6} --.

Line 45, change " 0.4×10^{-6} " to -- 0.4×10^{-6} --.

Column 75,

Line 35, change " 0.4×10^{-6} " to -- 0.4×10^{-6} --.

Line 37, change " 6.4×10^{-6} " to -- 6.4×10^{-6} --.

Column 76,

Lines 3 and 4, change "(b) polymerizing the core in an atmosphere substantially free from oxygen" to -- (b) polymerizing the core formulation in an atmosphere substantially free from oxygen to form a biocompatible lens having a core and surfaces; --.

Line 8, change "autoclaving lens" to -- autoclaving said lens --.

Line 25, change "wherein said ophthalmic lens" to -- wherein said biocompatible lens --.

Column 77,

Line 39, change "worn as extended wear lens that is worn for" to -- worn as an extended wear lens for --.

Line 61, change "continous" to -- continuous --.

Column 78,

Line 9, change "worn as extended wear lens that is worn for" to -- worn as an extended wear lens for --.

Column 79,

Line 12, change " 6.4×10^{-6} " to -- 6.4×10^{-6} --.

Line 14, change " 0.4×10^{-6} " to -- 0.4×10^{-6} --.

Line 47, change "continous" to -- continuous --.

UNITED STATES PATENT AND TRADEMARK OFFICE
CERTIFICATE OF CORRECTION

PATENT NO. : 6,951,894 B1
 DATED : October 4, 2005
 INVENTOR(S) : Nicolson et al.

Page 2 of 4

It is certified that error appears in the above-identified patent and that said Letters Patent is hereby corrected as shown below:

Column 80.

Line 18, change "absorption" to -- adsorption --.

Line 22, change " 0.4×10^{-6} " to -- 0.4×10^{-6} --.

Line 24, change " 6.4×10^{-6} " to -- 6.4×10^{-6} --.

Line 28, change "continous" to -- continuous --.

Line 49, change "less that about" to -- less than about --.

After line 49, add the following claims:

85. An extended wear contact lens comprising a core polymeric material and inner and outer surfaces that are more hydrophilic than said core polymeric material, said core polymeric material formed from a silicone copolymer which provides a high ion permeability and a high oxygen permeability; said silicone copolymer comprising an oxyperm polymerizable material, and an ionoperm polymerizable material; said core polymeric material having an oxygen permeability equal to or greater than 69 barrers; wherein said extended wear contact lens can be continuously worn for at least fourteen days on a human eye without substantial corneal swelling and without having substantial amounts of lipid adsorption.

86. A siloxane hydrogel contact lens comprising a core polymeric material having hydrophilically modified surfaces that are more hydrophilic than said core material, said hydrogel contact lens being suited to make contact with ocular tissue and ocular tissue and ocular fluids, said core polymeric material being formed from polymerizable materials comprising:

- (a) an oxyperm polymerizable material, and
- (b) an ionoperm polymerizable material,

wherein said lens has an oxygen permeability of at least about 69 barrers and an ion permeability characterized either by an Ionoflux Ion Diffusion Coefficient of greater than about $6.4 \times 10^{-6} \text{ mm}^2/\text{sec}$ or an Ionoton Ion Permeability Coefficient of greater than about $0.4 \times 10^{-6} \text{ cm}^2/\text{min}$ to enable the lens to move on the eye such that corneal health is not substantially harmed and wearer comfort is acceptable during a period of continuous contact with ocular tissue and ocular fluids, wherein said hydrogel contact lens is adapted for at least 14 days of continuous wear on a human eye without substantial corneal swelling and without having substantial amounts of lipid adsorption.

87. A biocompatible contact lens having an oxygen permeability of at least about 69 barrers and an ion permeability characterized by an Ionoton Ion Permeability Coefficient of greater than about $0.4 \times 10^{-6} \text{ cm}^2/\text{min}$, said lens comprising:

- (a) a polymeric core material in the shape of contact lens having an inner and outer surface; and
- (b) said surface of said core material being surface treated to form surfaces that are more hydrophilic than said core material;

UNITED STATES PATENT AND TRADEMARK OFFICE
CERTIFICATE OF CORRECTION

PATENT NO. : 6,951,894 B1
 DATED : October 4, 2005
 INVENTOR(S) : Nicolson et al.

Page 3 of 4

It is certified that error appears in the above-identified patent and that said Letters Patent is hereby corrected as shown below:

88. A biocompatible sterilizable contact lens having an oxygen permeability of at least about 69 barrers and an ion permeability characterized by an Ionoton Ion Permeability Coefficient of greater than about $0.4 \times 10^{-6} \text{ cm}^2/\text{min}$, said lens comprising:
- (a) a polymeric core material in the shape of contact lens having an inner and outer surface; and
 - (b) said surfaces of said core material being surface modified to form surfaces that are more hydrophilic than said core material;
- said lens having adequate movement on the eye without blinking to promote adequate tear exchange and without producing significant corneal swelling, without having substantial lipid adsorption, and without causing substantial wearer discomfort for a period of continuous contact for 30 days.
89. A contact lens comprising a polymeric material formed from at least:
- (a) an ionoperm polymerizable material comprising at least one of 2-hydroxyethyl methacrylate or N,N-dimethylacrylamide; and
 - (b) an oxyperm polymerizable material;
- wherein said lens has an oxygen transmissibility of at least about 70 barrers/mm and an ion permeability characterized either by (1) an Ionoton ion permeability coefficient of greater than about $0.25 \times 10^{-3} \text{ cm}^2/\text{sec}$, or (2) an Ionoflux diffusion coefficient of greater than about $1.3 \times 10^{-5} \text{ mm}^2/\text{min}$, wherein said ion permeability is measured with respect to sodium ions;
- wherein said lens is suitable for continuous, intimate contact with ocular tissue and ocular fluids while having adequate movement on the eye with blinking to promote adequate tear exchange and without producing significant corneal swelling, without having substantial amounts of lipid adsorption, and without causing substantial wearer discomfort during a period of wear of at least 24 hours.
90. The contact lens of claim 89 wherein said ionoperm polymerizable material comprises both 2-hydroxyethyl methacrylate and N,N-dimethylacrylamide.
91. The contact lens of claim 90 wherein said oxyperm polymerizable material comprises at least one of a siloxane containing macromer or a siloxane containing monomer.
92. The contact lens of claim 91 wherein said polymeric material is further formed from ethylene glycol dimethacrylate.
93. The contact lens of claim 92 wherein said lens is autoclaved without lowering either said oxygen transmissibility or said ion permeability below levels sufficient to maintain good corneal health and on-eye movement.
94. The contact lens of claim 92 wherein said period of wear is at least 4 days.
95. The contact lens of claim 92 wherein said period of wear is at least 7 days.
96. The contact lens of claim 89 further comprising polyvinylpyrrolidone at a surface of said lens.

UNITED STATES PATENT AND TRADEMARK OFFICE
CERTIFICATE OF CORRECTION

PATENT NO. : 6,951,894 B1
DATED : October 4, 2005
INVENTOR(S) : Nicolson et al.

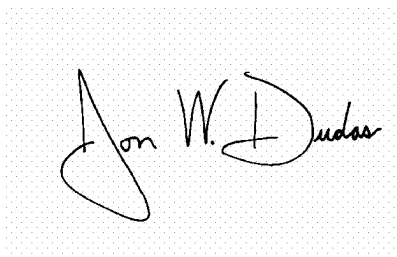
Page 4 of 4

It is certified that error appears in the above-identified patent and that said Letters Patent is hereby corrected as shown below:

97. The contact lens of claim 96 wherein said polyvinylpyrrolidone coats said surface of said lens.
98. The contact lens of claim 89 wherein said period of wear is at least 4 days.
99. The contact lens of claim 89 wherein said period of wear is at least 7 days.
100. The contact lens of claim 89 wherein said lens has an equilibrium water content of about 10 to about 30 weight percent.

Signed and Sealed this

Twenty-first Day of March, 2006

A handwritten signature in black ink on a light gray dotted background. The signature is written in a cursive style and appears to read "Jon W. Dudas".

JON W. DUDAS

Director of the United States Patent and Trademark Office